Carbon Nanotubes Inhibit the Free-Radical Cross-Linking of Siloxane Polymers

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ABSTRACT: Carbon nanotubes (CNTs) are found to inhibit the free-radical cross-linking of vinyl-terminated polydimethylsiloxane (PDMS) by trapping the free radicals in a CNT/PDMS composite. The cross-linking density values measured by swelling test, equilibrium stress-strain test, glass-transition temperature and Raman spectroscopy all decrease with the addition of CNTs. The inhibition effect is shown to be more significant with increased functionality and curvature in the CNTs used. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2014, 131, 40355.

INTRODUCTION

Since their discovery in 1991, carbon nanotubes (CNTs) have attracted great interest from various fields, the most promising of which is the field of CNT/polymer composites. The exceptional physical and chemical properties of CNTs make them ideal candidates for advanced filler materials in composites. For example, their high electrical conductivity and high aspect ratio can greatly decrease the percolation threshold of conductive plastics.[1] Their massive thermal conductivity may also be exploited to create thermally conductive composites.[2] In addition, their low density, superior Young's modulus,[3] and tensile strength[4] can dramatically enhance the mechanical properties of CNT-reinforced composites.

The prerequisite to preparing a CNT/polymer composite for these applications is that the CNTs do not interfere with the polymerization or cross-linking of the polymer matrix. For many years, this was simply assumed to be the case, given the graphitic nature of CNTs.[5] However, further studies on CNTs determined that they were not always inert. With a large area of sp[2]-hybridized structure and a high electron affinity, CNTs actually exhibit strong reactivity towards free radicals. This unique property has since been used in side-wall functionalization of CNTs,[6–9] elongation of polymer lifetime as free-radical trapping agents,[10] and antioxidant treatment for pathologies.[11]

Yet, it is not clear whether this reaction between CNTs and free radicals may affect free-radical cross-linking. The present study is aimed at understanding how the structure of CNTs could affect free-radical cross-linking in a CNT/polymer composite. A composite of multiwalled CNTs (MWCNTs) and vinyl-terminated polydimethylsiloxane (PDMS) is used as a model compound.

EXPERIMENTAL

Materials

Two types of MWCNTs were obtained from Chengdu Organic Chemistry, China. Both types were 10–20 μm long and had purity above 95%. CNT-A had a diameter of 8–15 nm, whereas CNT-B had a diameter of more than 50 nm. Graphite 230U was donated by Asbury Carbons. Wacker® V-20000 (average molecular weight: 48,000; vinyl content: 1.3%) was used as the PDMS matrix with dicumyl peroxide as the cross-linking initiator. Unless otherwise mentioned, the CNTs in CNT/PDMS composites were used as received, without any additional purification processes. HNO₃ treatment of CNTs was performed by mixing 5 g CNTs with a 250 mL 35% HNO₃ solution and refluxed for different time at 100°C. The obtained mixture was filtered and washed with deionized water. The treated CNTs were then dried under vacuum for 20 hours at 70°C and denoted as HNO₃-CNTs.

Additional Supporting Information may be found in the online version of this article.

Cross-Linking of PDMS and CNT/PDMS Composites

To prepare the CNT/PDMS composite, 2 g of PDMS and 0.03 g of dicumyl peroxide were first dissolved together in 20 mL toluene, while the CNTs were dispersed in toluene (8 mg/mL) by ultra-sonication (Aquasonic 75HT) for 1 hour. The CNT dispersion was then poured into the PDMS and mixed by ultra-sonication for an additional 3 hours. The homogenous mixture was then cast in a petri dish and dried under a fume hood for 24 hours. The resulting dry film was pressed into a Teflon mold and cross-linked at 150°C for 1 hour under 1.6 MPa pressure. Pure PDMS matrices were cross-linked under an identical procedure to the filled composites.

Characterization

Tensile strength and Young's modulus were measured using a typical tensile test setup (Instron microtester 5548). Samples were cut into a dumb-bell shape (28.75 mm × 4.75 mm, narrow portion 8.25 mm × 1.5 mm). The testing speed was set at 50 mm/min. The same setup was also used to measure the cross-linking density; however, a smaller extension rate of 10 mm/min was used to guarantee that the deformation reached equilibrium at any instant of the extension.

Swelling tests were performed by immersing 20 mm × 5 mm × 2 mm rectangular pieces of PDMS or CNT/PDMS composites in toluene for 5 days to allow thermodynamic equilibrium to be reached. The samples were then taken out of the solvent and placed in the fume hood for 10 days to dry. The weight and dimensions before swelling, after swelling, and after solvent evaporation were measured.

The glass transition temperature of cross-linked CNT/PDMS and pure PDMS was measured by dynamic mechanical analyzer (DMA, TA instrument 2890) using the film-tension mold.

A 5 mm × 3 mm × 2 mm film was initially cooled to −150°C using the liquid nitrogen cooling system, and then heated to room temperature at a rate of 5°C/min. The sample was oscillated at a constant frequency of 10 Hz with amplitude of 20 μm. The DMA T_g is determined to be the intersection of two tangent lines from the storage modulus curve.

Raman spectra of CNTs in the composites were obtained by a LabRAM ARAMIS Raman confocal microscope (HORIBA Jobin Yvon) equipped with a 532 nm diode-pumped solid state (DPSS) laser. Si wafer was used as a substrate.

The X-ray photoelectron spectroscopy (XPS) of CNTs was carried out with a Thermo K-Alpha XPS.

RESULTS AND DISCUSSION

Free-radical reaction is the oldest and one of the most widely used schemes in preparing PDMS elastomers. Vinyl-terminated PDMS can be cross-linked with a peroxide-based initiator at elevated temperature via free-radical reaction according to the reaction shown in Figure 1. The peroxide initiator decomposes and generates free radicals that can react with vinyl groups and initiate the cross-linking.

Carbon-based reinforcements are often added to elastomers to improve their mechanical properties. CNTs are reported to be more efficient reinforcement than conventional fillers, because of their high aspect ratio and intrinsic mechanical robustness.[12] Young's modulus and tensile strength of a CNT/PDMS composite usually increases with increasing loading of CNTs. For CNT-B, it is indeed this case [Figure 2(b)]. The tensile strength and Young's modulus increase by 1.5 times and 2.5 times, respectively, when increasing the CNT loading from 1 to 20 wt %. However, for the CNT-A/PDMS composite, a totally opposite
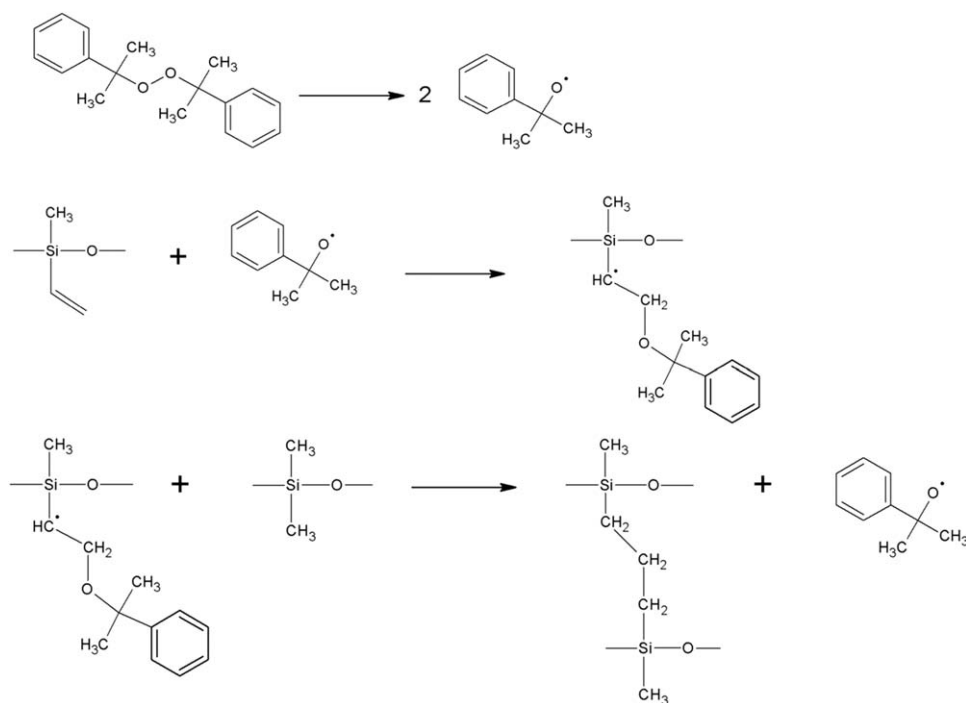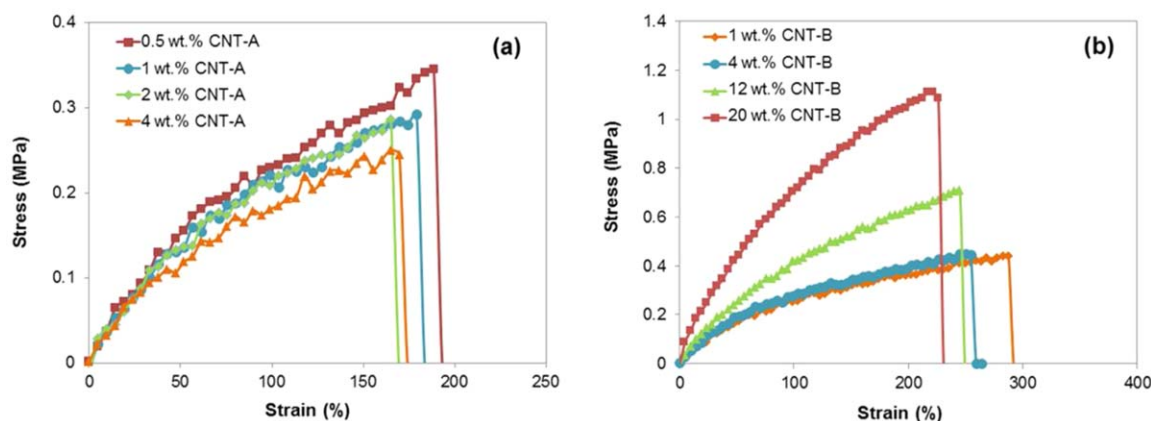

Figure 1. Cross-linking mechanism of vinyl-terminated PDMS through free–radical reaction.

Figure 2. Tensile stress–strain curves of: (a) CNT-A/PDMS composites and (b) CNT-B/PDMS composites with various CNT loadings. The concentration of CNTs refers to weight percentage, which is used throughout the whole text. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

trend is observed [Figure 2(a)]; the tensile strength and Young's modulus decrease with increasing CNT loading. This leads to an investigation into the possible adverse effects of CNT-A on the cross-linking of PDMS.

The cross-linking density of CNT-A/PDMS composites is measured by swelling test, equilibrium stress–strain test, glass transition temperature measurement and Raman spectroscopy. In a swelling test, CNT-A/PDMS composite samples are immersed in toluene. The samples absorb toluene and swell, until an equilibrium between the thermodynamic tendency to swell and the retractive forces from the cross-linked network is reached. The cross-linking density can be calculated from the swelling phenomenon by Flory-Rehner equation[13]

$$N = -\frac{1}{2V_s} \frac{\ln(1-V_r) + V_r + \chi V_r^2}{V_r^{1/3} - V_r/2} \qquad (1)$$

where N is the moles of effective cross-links in a unit volume; V_s and V_r represent the molar volume of toluene and the volume fraction of PDMS in the swollen gel, respectively. χ is the polymer–solvent interaction parameter. For PDMS and toluene, χ is 0.465 and the molar volume of toluene V_s is 106.29 mL/mol.[14] With CNT fillers, the volume fraction of PDMS in swollen gel is given by (derivation details in supporting information)

$$V_r = \frac{S_p - \frac{S_e}{(1-\varphi)}\left(\frac{I-F}{I}\right)}{S_p + S_s\left(\frac{S-F}{I}\right) - S_e\left(\frac{I-F}{I}\right)} \qquad (2)$$

where I is the initial weight, S is the swollen weight, F is the final dry weight, S_p is the initial specific volume of the composite, S_e is the specific volume of the extract, S_s is the specific volume of toluene solvent, and φ is the volume fraction of the filler.[15] The effective cross-linking density of CNT-A/PDMS composites with different CNT loadings is calculated according to eqs. (1) and (2) and the results are shown in Figure 3(a).

In cases where the fillers do not affect the curing process, the measured cross-linking density of the composite will be slightly higher than that of the pure resin. This can be explained by several mechanisms: (1) the fillers can pose steric hindrance to polymer chain movement during swelling; (2) the physical

interaction between the fillers and matrix contributes to the total retraction force of the polymer network[16]; and (3) the polymer chain and fillers (especially CNTs) form physical entanglements that restrict the swelling displacement.[17] However, as shown in Figure 3(a), the effective cross-linking density of the composites decreases with an increase in the amount of filler. Even with 0.5 wt % CNT-A, the cross-linking density decreases 1/3 from 90 to 59 mol/m³. When the CNTs' concentration increases further to 10 wt %, the cross-linking density drops to 26 mol/m³, 1/3 of the original value. This dramatic decrease in the cross-linking density indicates that the carbon fillers may have a negative role on the cross-linking process of a PDMS resin.

Equilibrium stress–strain measurement is another way to determine the cross-linking density from the Mooney-Rivlin equation:

$$\frac{\sigma}{2(\lambda - \lambda^{-2})} = C_1 + \frac{C_2}{\lambda} \qquad (3)$$

where σ and λ represent the engineering stress and the extension ratio, respectively.[13] C_1 and C_2 are two elastic constants. C_1 is proportional to the effective cross-linking density N_c given by

$$C_1 = N_c RT \qquad (4)$$

where R is the gas constant and T is temperature. Thus a plot of $\sigma/(2(\lambda - \lambda^{-2}))$ versus $1/\lambda$ can be used to determine the constant C_1 and thus the cross-linking density. To guarantee that the deformation is reaching equilibrium at any instant, a small extension rate of 10 mm/min was used in tensile tests, and only the data approaching the break point was analyzed. The results are shown in Figure 3(b). The values of the cross-linking density from stress–strain measurements are quite consistent with those from the swelling test. The cross-linking density drops 1/3 with 0.5 wt % CNT-A, then stays relatively stable from 0.5 to 5 wt % CNTs, likely as a result of a trade-off between an increase in physical entanglement and the loss of chemical cross-links. When the CNT loading is above 5 wt %, the cross-linking density continues to drop to 33 and 6 mol/m³ for 10 wt % loading and 20 wt % loading, respectively.

The glass transition temperature (T_g) can be used as an indicator of the cross-linking density, where elastomers with higher
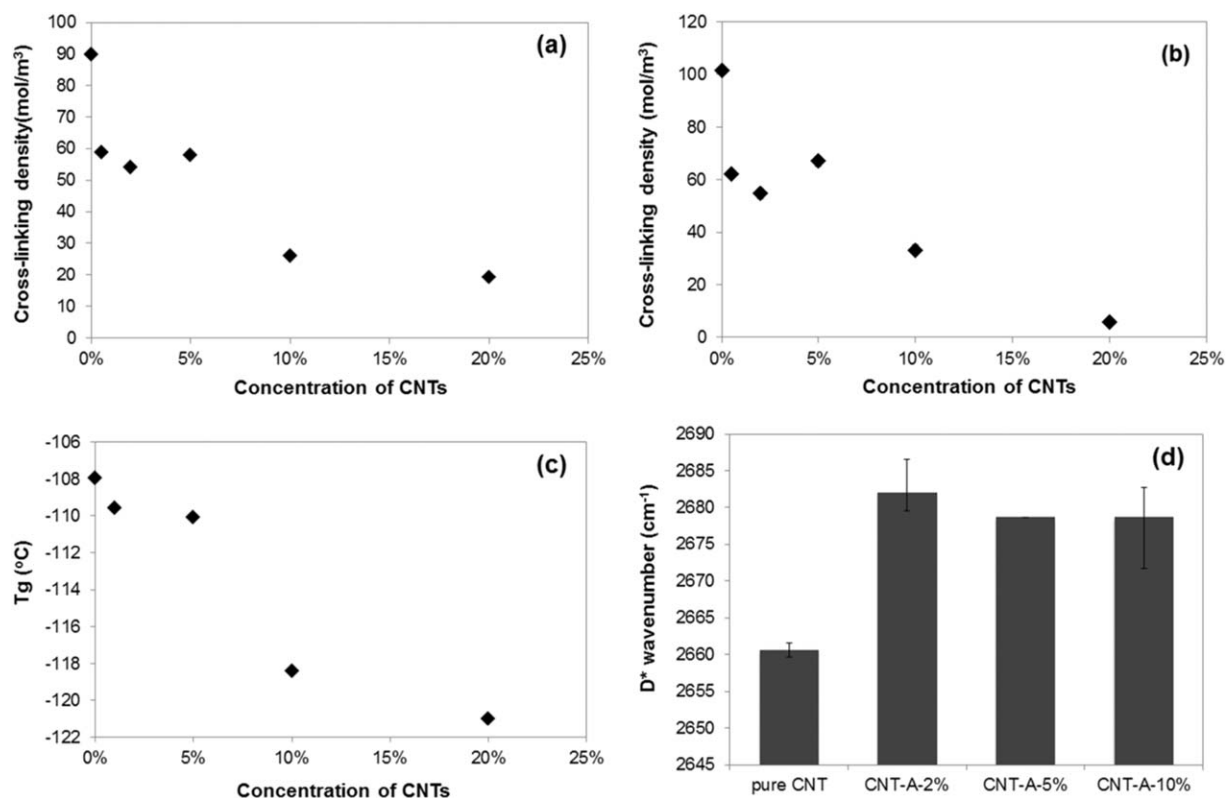
Figure 3. Effective cross-linking densities of CNT-A/PDMS composites with different filler loadings determined by (a) swelling test, (b) equilibrium stress–strain measurements. (c) Glass transition temperature of the CNT-A/PDMS composites as a function of CNT concentration. (d) D* wavenumber in Raman spectra of CNTs in CNT-A/PDMS composites.

cross-linking density usually have a higher T_g. Here, T_g of CNT/PDMS composites with different concentrations were measured by DMA and the result is shown in Figure 3(c). For pure PDMS, it has a T_g of $-108°C$, but with adding CNT-A into the composite, the T_g decreases monotonically with increasing the CNT-A concentration. T_g decreases to $-110°C$, -118 °C, and $-121°C$ after adding 5 wt.%, 10 wt.%, and 20 wt.% of CNT-A, respectively. The decrease in T_g suggests a decreased cross-linking density after adding CNT-A, which is consistent with results shown in Figure 3(a,b).

Raman spectroscopy has also been used to characterize the cross-linking in CNT/polymer composites. The second-order overtone of the D band, the D* band, is very sensitive to any perturbation in the load transfer at the interface between the CNTs and the polymer matrix.[18,19] Zhao et al. took advantage of the Raman shift induced by polymer contraction in the cross-linking process and found a positive correlation between the D* band up-shift and the cross-linking density.[18] For this study, the D* shifts of the CNT-A/PDMS composites of different filler loadings were compared [Figure 3(d), Raman spectra shown in supporting information]. A filler loading as low as 2 wt % will lead to a 22 cm^{-1} up-shift of the D* band, resulting from the contraction of the PDMS matrix after cross-linking, which imposes a compression force to the individual CNT. However, with the increasing CNT concentration, we observed a down-shift of D* band rather than an up-shift, indicating that the cross-linking density actually decreases with more CNTs.

All the above results suggest that CNTs may adversely affect the free-radical cross-linking process of the PDMS matrix. This result is not surprising considering fullerenes have also been reported to retard the free-radical polymerization reaction of methyl methacrylate, styrene, vinyl acetate, etc.[20–22] The retardation was attributed to fullerene's strong electron affinity of approximately 2.65 eV, and to its ability to accommodate free radicals by forming stable radical adducts.[23,24]

With a similar sp^2-hybridized structure and even stronger electron affinity than fullerene,[25] CNTs are expected to show a similar spin-trapping capability. As early as 2003, Watts et al. proposed that CNTs could act as antioxidants, i.e. radical-trapping agents, to retard the aging of polystyrene, polyethylene, polypropylene and poly(vinylidene fluoride).[10] In addition, intensive studies have been conducted to modify the CNTs' surface using free radicals.[6–9] Researchers make use of the addition reaction of free radicals with CNT double bonds to graft various functional groups to the CNTs. These radicals include alkyl radicals and peroxide radicals, indicating that CNTs can accept a wide range of radicals. The PDMS in this study is cross-linked via a free-radical reaction. Therefore, it is reasonable to assume that the decreased cross-linking density of PDMS results from the trapping of free radicals by CNT-A during curing.

However, only some CNTs (such as CNT-A in Figure 2) demonstrate this effect, whereas others (such as CNT-B) do not.

Table I. Carbon/Oxygen Atomic Ratio of CNTs Measured by XPS

Treatment time (mins)	C/O
CNT-A	39.16
CNT-B	24.71
CNT-A, HNO$_3$-10 min	35.10
CNT-A, HNO$_3$-30 min	22.53
CNT-A, HNO$_3$-120 min	4.99

This raises the question, what structural characteristics in CNTs determine their reactivity towards free radicals?

One possible determining factor is the functionality of CNTs. CNTs contain functional groups either from the synthesis and/or the purification processes. It has been reported that the functional groups, especially hydroxyl and carboxyl groups, increase the free-radical trapping activity with respect to pristine CNTs.[26,27] To demonstrate that the functionality in CNTs may increase the reactivity towards free radicals and decrease the cross-linking density of PDMS, CNT-A was treated with HNO$_3$ at 100°C for different durations (10, 30, and 120 mins). The XPS results (Table I) show that longer acid treatment time does introduce more oxygen content, i.e. functional groups in CNTs. The effect of the amount of functional groups is evident (Figure 4). The cross-linking density decreased dramatically with increasing the acid treatment time. The cross-linking density also decreases with increasing CNT concentration. That is, the cross-linking density is strongly dependent on the total amount of functional groups in the CNTs. For CNTs treated longer than 30 min, the CNT/PDMS cannot cure, even at a low CNT loading of 5 wt % (the composites completely dissolved in toluene during the swelling test). Therefore, functional groups on the CNT surfaces can significantly hinder the free-radical cross-linking of a PDMS matrix. When preparing CNT/polymer composites, over-functionalizing CNTs during purification should be avoided if they are to be used in polymer matrices that are cured by free-radical reactions.

Another possible determining factor is the curvature of the CNTs.[28] Peng et al. observed less reactivity of the CNTs with free radicals than that of fullerenes, which was attributed to the smaller curvature of CNT sidewalls built from graphene cylinders.[8] In one study of cyclopolyenes, a high curvature was found to lead to the stabilization of the Lowest Unoccupied Molecular Orbital (LUMO) and an increase in electron affinity.[29] If we regard CNTs as large-area cyclopolyenes, increasing the curvature of the graphene sheet in the CNTs will increase the electron affinity and hence increase the addition reaction rate. In addition, during the study of fullerene's reaction with benzyl radicals, it was found that the curved surface of fullerenes may facilitate the bulky benzyl groups in shielding and stabilizing the radicals.[28] In the present study, three fillers with different curvatures were investigated. CNT-A with a diameter of 8–15 nm represents the highest curvature; CNT-B with a diameter of more than 50 nm represents the medium-curvature; and graphite represents the lowest, i.e. zero curvature. The cross-linking densities calculated by the swelling tests and stress-strain measurements of PDMS composites with these three fillers are shown in Figure 5. As theorized, CNT-A demonstrates the highest reactivity to trap the free radicals and decrease the cross-linking density of PDMS. Graphite has little influence on the cross-linking density due to its zero curvature. CNT-B/PDMS composites show increased cross-linking density when the filler loading increases, indicating that large-diameter CNTs have little effect on the curing of PDMS and the "physical entanglement" between PDMS chains and CNT-B increases the total cross-linking density. Note that the comparison is predicated on the assumption that all parameters other than the diameter are the same for the three fillers. However, in real cases, the functionality cannot be so precisely controlled. XPS results show that CNT-B has a C/O ratio of 24.71 while CNT-A has a C/O ratio of 39.16, indicating that CNT-B may contain more functional groups than CNT-A does. As CNT-A still shows a more significant reactivity towards free radicals, the determining factor here may be the curvature of CNTs.

CONCLUSIONS

In conclusion, this study found that CNTs inhibit the free–radical cross-linking of PDMS in a CNT/PDMS composite. The
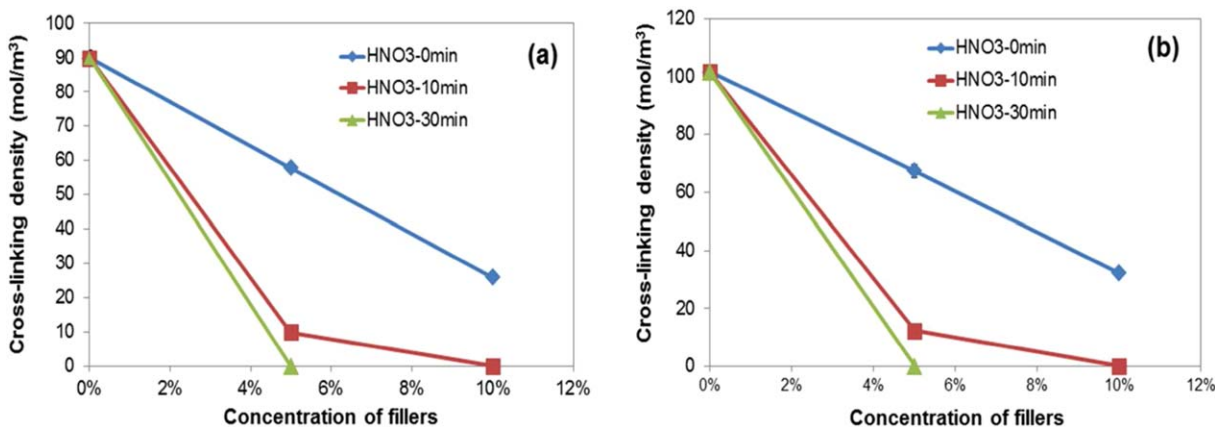
Figure 4. Effective cross-linking densities of CNT-A/PDMS composites determined by (a) swelling test and (b) equilibrium stress–strain measurements. The CNT-A is treated with HNO$_3$ at different durations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
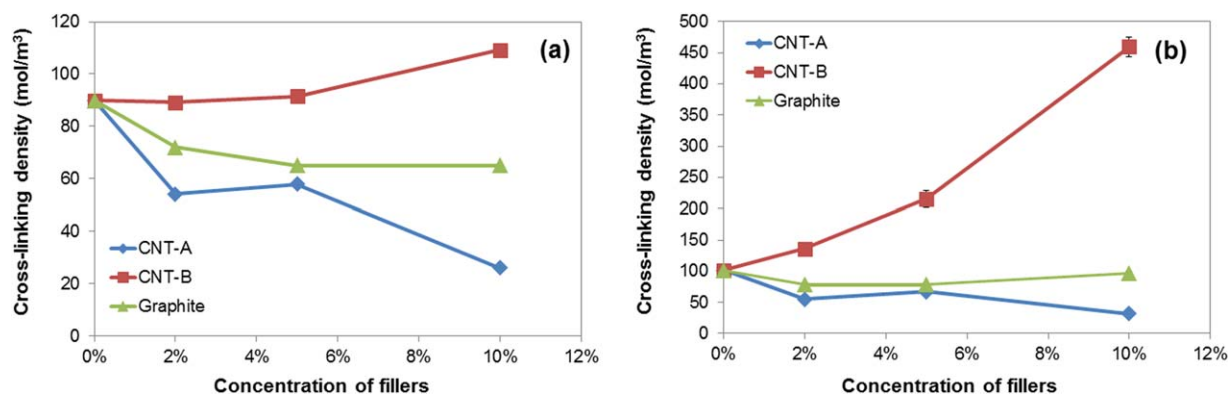
Figure 5. Effective cross-linking densities of CNT-A/PDMS, CNT-B/PDMS and graphite/PDMS composites with different filler loadings determined by (a) swelling test and (b) equilibrium stress–strain measurements. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

inhibition effect is more significant for CNTs with more functional groups and smaller diameters.

REFERENCES

1. Kilbride, B. E.; Coleman, J. N.; Fraysse, J.; Fournet, P.; Cadek, M.; Drury, A.; Hutzler, S.; Roth, S.; Blau, W. J. *J. Appl. Phys.* **2002**, *92*, 4024.

2. Lin, W.; Moon, K. S.; Wong, C. P. *Adv. Mater.* **2009**, *21*, 2421.

3. Wong, E. W.; Sheehan, P. E.; Lieber, C. M. *Science* **1997**, *277*, 1971.

4. Yu, M. F.; Lourie, O.; Dyer, M. J.; Moloni, K.; Kelly, T. F.; Ruoff, R. S. *Science* **2000**, *287*, 637.

5. Bottini, M.; Bruckner, S.; Nika, K.; Bottini, N.; Bellucci, S.; Magrini, A.; Bergamaschi, A.; Mustelin, T. *Toxicol. Lett.* **2006**, *160*, 121.

6. Peng, H.; Reverdy, P.; Khabashesku, V. N.; Margrave, J. L. *Chem. Commun.* **2003**, 362.

7. Ying, Y.; Saini, R. K.; Liang, F.; Sadana, A. K.; Billups, W. E. *Org. Lett.* **2003**, *5*, 1471.

8. Peng, H.; Alemany, L. B.; Margrave, J. L.; Khabashesku, V. N. *J. Am. Chem. Soc.* **2003**, *125*, 15174.

9. McIntosh, D.; Khabashesku, V. N.; Barrera, E. V. *J. Phys. Chem. C* **2007**, *111*, 1592.

10. Watts, P. C. P.; Fearon, P. K.; Hsu, W. K.; Billingham, N. C.; Kroto, H. W.; Walton, D. R. M. *J. Mater. Chem.* **2003**, *13*, 491.

11. Marcano, D. C.; Bitner, B. R.; Berlin, J. M.; Jarjour, J.; Lee, J. M.; Jacob, A.; Fabian, R. H.; Kent, T. A.; Tour, J. M. *J. Neurotraum.* **2013**, *30*, 789.

12. Coleman, J. N.; Khan, U.; Blau, W. J.; Gun'ko, Y. K. *Carbon* **2006**, *44*, 1624.

13. Hamed, G. R. In Engineering with Rubber—How to Design Rubber Component; Gent, A. N., Ed.; Hanser: New York, **1992**; Chapter 2.

14. Treloar, L. R. G. The Physics of Rubber Elasticity; Clarendon Press: Oxford, **2005**.

15. French, D. M. *J. Appl. Polym. Sci.* **1980**, *25*, 665.

16. Maxwell, R. S.; Cohenour, R.; Sung, W.; Solyom, D.; Patel, M. *Polym. Degrad. Stabil.* **2003**, *80*, 443.

17. Verge, P.; Peeterbroeck, S.; Bonnaud, L.; Dubois, P. *Compos. Sci. Technol.* **2010**, *70*, 1453.

18. Zhao, Q.; Tannenbaum, R.; Jacob, K. I., *Carbon* **2006**, *44*, 1740.

19. Linton, D.; Driva, P.; Sumpter, B.; Ivanov, I.; Geohegan, D.; Feigerle, C.; Dadmun, M. D. *Soft Matter.* **2010**, *6*, 2801.

20. Kirkwood, K.; Stewart, D.; Imrie, C. T. *J. Polym. Sci. Polym. Chem.* **1997**, *35*, 3323.

21. Chen, Y.; Lin, K. -C. *J. Polym. Sci. Polym. Chem.* **1999**, *37*, 2969.

22. Seno, M.; Maeda, M.; Sato, T. *J. Polym. Sci. Polym. Chem.* **2000**, *38*, 2572.

23. Liu, J.; Rinzler, A. G.; Dai, H.; Hafner, J. H.; Bradley, R. K.; Boul, P. J.; Lu, A.; Iverson, T.; Shelimov, K.; Huffman, C. B.; Rodriguez-Macias, F.; Shon, Y.-S.; Lee, T. R.; Colbert, D. T.; Smalley, R. E. *Science* **1998**, *280*, 1253.

24. Morton, J. R.; Preston, K. F.; Krusic, P. J.; Hill, S. A.; Wasserman, E. *J. Phys. Chem. C* **1992**, *96*, 3576.

25. Buonocore, F.; Trani, F.; Ninno, D.; Matteo, A. D.; Cantele, G.; Iadonisi, G. *Nanotechnology* **2008**, *19*, 025711.

26. Francisco-Marquez, M.; Galano, A.; Martinez, A. *J. Phys. Chem. C* **2010**, *114*, 6363.

27. Martnez, A.; Francisco-Marquez, M.; Galano, A. *J. Phys. Chem. C* **2010**, *114*, 14734.

28. Krusic, P. J.; Wasserman, E.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *Science* **1991**, *254*, 1183.

29. Sola, M.; Mestres, J.; Duran, M. *J. Phys. Chem. C* **1995**, *99*, 10752.